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Growth and characterization of benzylic amide [2]catenane thin films

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Abstract

We report here the first results on the thin-film growth of benzylic amide catenanes. The films were deposited onto gold single crystals by two different methods: by sublimation under ultra-high vacuum and by dipping of the substrate into a solution of the catenane. Sublimation yielded well-ordered films (domain diameter ~100 Å) while dipping produced disordered films. The vibrational and electronic properties of these films were investigated by high-resolution electron energy loss spectroscopy (HREELS) as a function of film thickness. The vibrational spectra indicate that the first layer of catenanes is chemisorbed.

Keywords: Catenane; Thin film; Vibrational spectrum; Electronic transition

1. Introduction

The synthesis and property characterization of supramolecular and molecular interlocked chemical objects is attracting a remarkable amount of interest [1–7], deriving on one hand from the often elegant strategies developed for their preparation, and on the other from practical, if not yet technological, considerations. The latter are based on the observation that several of the interlocked structures prepared so far can change the relative positions of their component parts under external stimulus. Interlocked molecular rings, or catenanes, first made available through the pioneering work of Stoddart and Sauvage [2–6], occupy a special place in this category of new materials since their macrocycles can circumrotate one another like the rings of a macroscopic chain. This adds a degree of freedom not available to other systems that may find a role in the development of nanoscale devices such as molecular shuttles, switches and information storage systems (for review on electrooptically switchable catenanes, see [7]). An important milestone on the way towards a possible future application of catenanes is the development of techniques to grow ordered arrays of these molecules. A first step in this direction is outlined below.

Here we report the first study of thin film growth of the prototypical benzylic amide[2]catenane. This catenane, prepared through a one-step self-assembly process serendipitously discovered at UMIST [8,9], consists of eight phenyl groups, eight amide groups and four methylene groups which form two macrocycles as shown in Fig. 1. The molecular architecture of this molecule and its structure in the solid state as determined by X-ray diffraction [8], are maintained through intra- and intermolecular hydrogen bonds and by π-type interactions between the aromatic rings. In this work we show (a) that the catenane structure remains intact when the molecule sublimates; (b) that its adsorption on a metallic surface can influence the solid state structure of a growing film leading to well-ordered arrays of molecules; but that (c) this template effect of the substrate is limited to the very first layers as deduced from the poorer crystalline order of thicker films. These results derive from

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the characterization of the structural, vibrational and electronic properties of catenane thin films by HREELS.

2. Experimental

The HREELS experiments were performed in a two-chamber ultra-high-vacuum system equipped with a high-resolution spectrometer (ISA-Riber). The base pressure in the analysis and preparation chambers was 5×10^{-10} and 2×10^{-10} Torr, respectively. The spectrometer consists of two hemispherical electrostatic selectors, one acting as monochromator, the other as analyzer, and the energy of the incident electron beam can be varied from 0 up to 150 eV. The instrumental resolution was set to 11–15 meV for the vibrational spectra and to 0.03–0.05 eV for the study of the electronic structure. The spectrometer had an acceptance angle of 1.2°. All the spectra reported here are normalized to the area under the spectrum if they were recorded in the specular geometry or to that of the corresponding specular spectrum if they were recorded off-specular.

The catenane studied in this work is [2] (1,7,14,20-tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(1′,7′,14′,20′-tetraaza-2′,6′,15′,19′-tetraoxo-3′,5′,9′,12′,16′,18′,22′,25′-tetrabenzocyclohexacosane) which was synthesized as described in Ref. [8]. Two methods were used to prepared the films: dipping and the sublimation under ultra-high vacuum (UHV).

2.1. Dipping

The substrate, an Au(110) single crystal was cleaned by sputtering annealing cycles until no contaminants were detected in the HREELS spectrum and a clear (1×2) low-energy electron diffraction pattern was obtained. The crystal was then removed from the vacuum and immediately dipped in an approximately 10^{-4} molar methanol solution. The dipping time initially used was 2 h but the films produced in this way were too thick and developed charging effects during the analysis. The time was thus reduced to 5 min for the films presented here. Each sample was dried by an argon flux before its reintroduction into the UHV chamber.

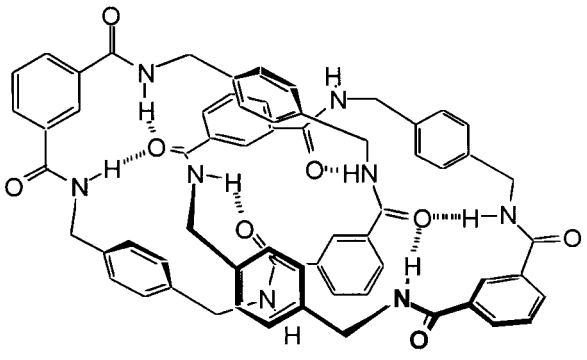

Fig. 1. Schematic drawing showing the X-ray crystal structure of the [2]catenane. Of particular interest are the bifurcated hydrogen bonds responsible for this particular architecture.

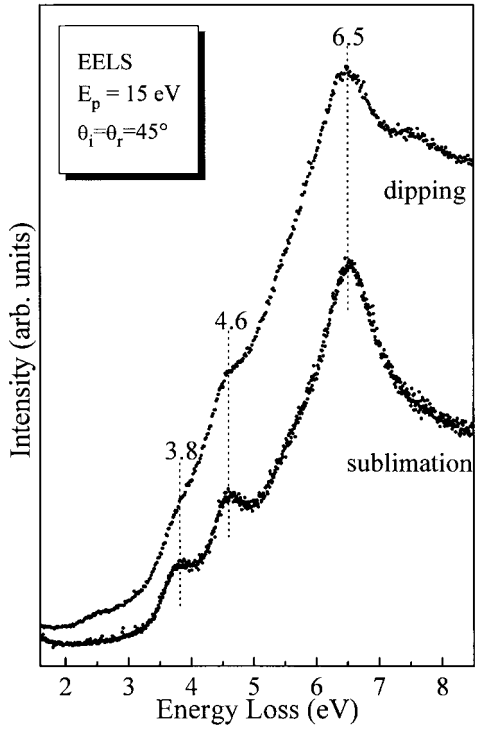

Fig. 2. EELS spectra recorded in specular geometry at 15 eV of a film prepared by dipping and a 70-Å film prepared by sublimation.

2.2. Sublimation

An Au(111) single crystal, cleaned as previously mentioned, was used as substrate. The catenane was sublimed at about 190°C from a Knudsen cell with a quartz crucible topped with a 1.3 mm stainless-steel collimator. The cell was previously outgassed up to about 250°C. The deposition rate was monitored by a quartz microbalance.

Since the catenane decomposes when heated in air [8,9] to high temperature, its stability during sublimation in UHV had to be established. In order to check the absence of catenane degradation during sublimation we first deposited an approximately 70-Å thick film. We have then compared the electron energy loss (EELS) spectrum of this sample with the one of a film prepared by dipping (Fig. 2). The spectroscopic features are discussed later in this paper, here it is important to note that these two spectra are identical showing that the catenane sublimes without degradation at 190°C.

The 70-Å thick film was annealed at 150°C for 15 min, causing a partial desorption. The sample obtained in this way will be called layer 1 throughout this paper. Three successive depositions were made on layer 1. Layer 2 corresponds to a deposition of 20 min on layer 1, layer 3 corresponds to a deposition of 20 min on layer 2 and layer 4 corresponds to a deposition of 30 min on layer 3. During the

depositions of layer 2, 3 and 4, the substrate was held at 100°C.

3. Results and discussion

3.1. Dipping

Fig. 3 shows the HREELS spectrum of the [2]catenane deposited by dipping onto an Au(110) single crystal. One can see several broad losses at 68, 130, 170, 208 and 364 meV: the peaks at 130 and 170 meV correspond to deformations of the phenyl groups and the one at 364 meV to the C–H stretching. The loss at 208 meV is assigned to the C=O stretching of the amide groups, while the shoulder at 68 meV corresponds to a deformation of the phenyl groups or a collective mode. The attribution of the losses is quite difficult because catenanes are complex molecules which have a large number of vibrational modes: this catenane is composed of 136 atoms and has no symmetry, so there are thus 402 fundamental modes that can contribute to the HREELS spectrum. However, for these films the attribution is further impeded by the low resolution (24 meV). This low resolution, together with the absence of a preferred scattering direction for the elastically scattered electrons, are indicative of a poor crystalline quality of the film prepared by the dipping. Films produced by this method on a Au(110) substrate are therefore not promising for a technological application.

3.2. Sublimation

The HREELS spectrum of the four layers of increasing thickness recorded in the specular geometry are shown in Fig. 4. One can immediately see the better resolution (11 meV) obtained, compared to the film prepared by dipping (24 meV). This shows a good organization of the films prepared by sublimation. Several losses can been observed on the spectra. The one at 60 meV corresponds to the Au–O stretching [10]. The observation of this vibration suggests

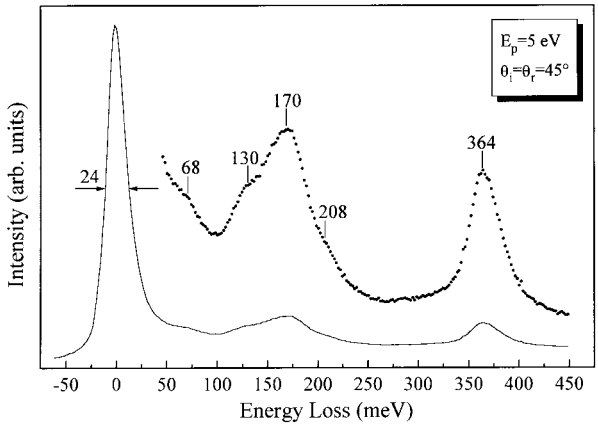

Fig. 3. HREELS spectrum recorded in specular geometry at 5 eV on a film prepared by dipping on an Au(110) single crystal. Scaling factor = 5.

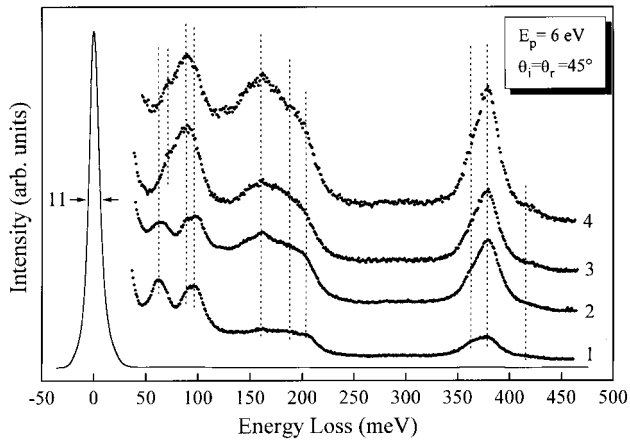

Fig. 4. HREELS spectra recorded in specular geometry at 6 eV on the four layers of increasing thickness grown by sublimation on the Au(111) single crystal. Scaling factor = 72.

that the catenane is chemisorbed on the Au(111) via the carbonyl moiety of the amide groups. The interpretation of this peak is supported by the fact that it disappears when the film thickness increases, in agreement with its interfacial nature. The losses at 70, 89, 96, 162 and 188 meV are associated to deformations of the phenyl and methylene groups. At 204 meV one can observe the C=O stretching mode of the amide group. The losses at 362 and 379 meV correspond to the aliphatic and aromatic C–H stretching, respectively. Finally, one can see the N–H stretching mode at 415 meV. The resolution obtained for layers 1 and 2 is 11 meV and only 15 meV for layers 3 and 4. This indicates that those are slightly less ordered than the two first ones. This point will be also demonstrated later based on the angular dependencies of the elastic peak intensity. One can also say that the HREELS spectra of the catenane recorded in specular geometry are strongly influenced by the film thickness. The catenane growth occurs thus differently if the molecules adsorb on the Au(111) single crystal surface or on a pre-existent catenane layer. The gold substrate seems to act as a template in the beginning of

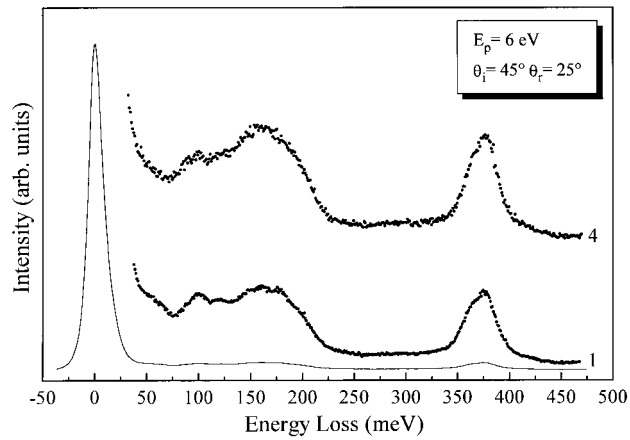

Fig. 5. HREELS spectra recorded in off-specular geometry at 6 eV on layers 1 and 4, both grown by sublimation. Scaling factor = 10.

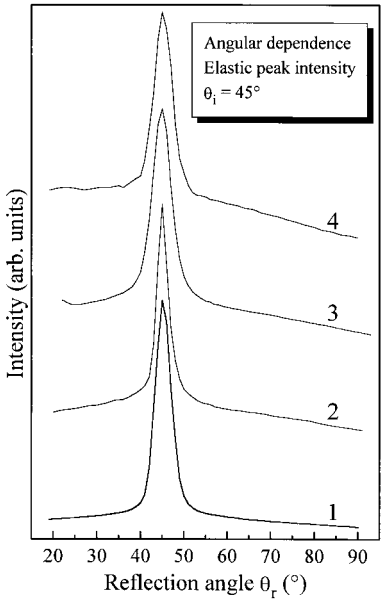

Fig. 6. Angular dependence of the elastic peak intensity recorded on the four layers grown by sublimation.

the growth inducing a better overlayer ordering. These changes in the vibrational structure are presumably due to a different orientation and not to a modification of the catenane structure itself since the HREELS spectra recorded in off-specular geometry on layers 1 and 4 are almost identical (Fig. 5). The comparison between the specular and the off-specular spectra of layers 1 and 4 can yield varied information. Firstly, one can see that the losses at 60, 89 and 96 meV disappear almost completely in the off-specular spectra. This shows that these modes are dipole-active, their intensity dropping drastically out of the specular direction. Secondly, the great difference between the spectra of Figs. 4 and 5 indicates that layers 1 and 4 are well ordered. Indeed, the HREELS theory tells us that in order to observe a difference between specular and off-specular spectra, the surface probed must be flat and have a good crystalline order.

More information on the crystalline quality of the different films can be obtained by measuring the angular dependencies of the elastic peak intensity. The elastically scattered electrons correspond in fact to the (0,0) Bragg beam and its width is related to the size of the domains. Assuming round domains, one can estimate their diameter by using [11]:

$$D \cong \frac{\lambda}{2\Delta\theta\cos\theta}$$

where $\Delta\theta$ is the full width at half maximum of the angular dependence corrected by the instrumental broadening, θ is the reflection angle and λ is the wavelength associated with the probing electrons. The angular dependencies measured on the four layers are presented on Fig. 6. Layer 1 gives a domain size of 65 Å, a value which is relatively small but can be justified if one assumes that this film corresponds to just a fraction of a monolayer, covering only partly the gold substrate. The domain diameter of layer 2 is 106 Å. This larger value indicates that the new growth proceeds in a crystalline way and that layer 2 is more uniform, the catenane covering now the whole Au(111) surface. The layers 3 and 4 have a domain size of 55 and 56 Å, respectively. This shows that the growth continues in a slightly more disordered way for the molecules adsorb now on a catenane layer and no more on the gold substrate. This illustrates once more the template effect played by the Au(111) single crystal.

In addition to the vibrational structure of the four layers, we have studied their electronic structure by EELS. Fig. 7 shows the EELS spectra recorded at 15 eV on layers 1 and 4. One can see four losses at 2.6, 3.8, 4.6 and 6.5 eV. The latter three losses are characteristic of the catenanes while the first one is not, as it is absent in the thick catenane film shown in Fig. 2. The 2.6 eV feature is in fact the Au(111) surface plasmon. This gold plasmon is nearly the dominant feature in the spectrum of layer 1, confirming the small thickness of this film. To interpret the electronic structure of the catenane, the EELS data have been compared with CNDO/S calculations [12]. The theory assigns the first two losses to dipole forbidden singlet–singlet transitions delocalized over the whole molecule and the 6.5 eV feature to a dipole allowed singlet–singlet transition centered on the phenyl rings. The variation of the loss intensities with primary energy of the electrons confirms this assignment (A.M. Brower, W.J. Buma, M. Fanti, et al., unpublished data). Fig. 7 clearly shows that the losses proper to the catenane are at the same position for all films. This suggests that the electronic structure of the catenane is not dramatically affected by the adsorption on the Au(111) surface.

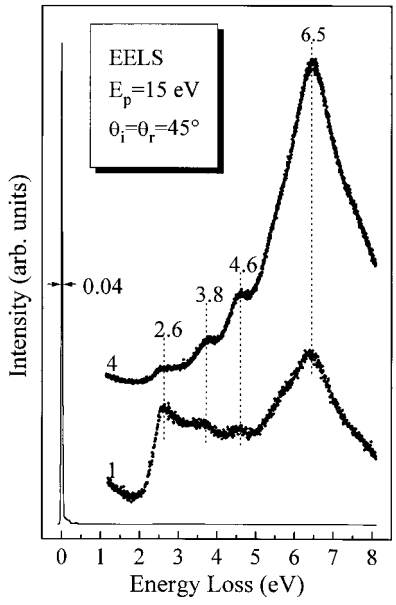

Fig. 7. EELS spectra recorded at 15 eV on layer 1 (scaling factor 340) and 4 (scaling factor 85), both grown by sublimation. The layer 1 spectrum is blown up in order to show the losses clearly.

4. Conclusions

We have tested two methods to grow ordered catenane thin films: dipping and sublimation under ultra-high vacuum. The first methods produced disordered films on Au(110) which have been useful to prove the absence of degradation of the catenane during sublimation. However, growth by sublimation yields ordered films on Au(111). Unfortunately, the order decreases when the layer thickness increases. The angular dependencies of the elastic peak intensity and the HREELS specular spectra recorded on the four layers lead us to think that the monolayer coverage should be close to layer 2. We have shown that the Au(111) single crystal has a template effect on the growth of very thin films. The observation of the Au–O vibration in the HREELS spectra of the very thin layers suggests that the catenane is chemisorbed on this substrate via its C=O moieties. The vibrational properties change strongly with the film thickness, revealing a different orientation of the catenane. The electronic properties, on the other hand, are not significantly influenced by the adsorption.

Acknowledgements

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